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## Generation, Diffusivity, and Quenching of Singlet Oxygen in Polymer Matrixes Investigated via Chemiluminescence Methods

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Singlet oxygen ( $^1\text{O}_2$ ) is generated in films of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by decomposition of a naphthalene 1,4-endoperoxide. Inclusion of bis(2,2'-biphenylene)ethylene (A) in such polymer films results in chemiluminescence that is identical with fluorenone fluorescence. This chemiluminescence is decreased by addition of singlet oxygen quenchers (under conditions that photoexcited fluorenone fluorescence would not be quenched). An investigation of the chemiluminescence intensity as a function of the concentration of A allows determination of the diffusivity of  $^1\text{O}_2$  in the polymer films, and the quenching of chemiluminescence intensity as a function of added quencher allows determination of the rate constants for quenching of  $^1\text{O}_2$  in the polymer films.

### Introduction

Singlet oxygen  $^1\text{O}_2$  has been suggested as an important contributor to thermal and photochemical degradation of polymers.<sup>1</sup> In spite of a vast and ever-expanding literature, neither the method of generation of  $^1\text{O}_2$  nor the details of the chemical pathways leading to polymer disintegration are known with certainty. We report a simple, nonphotochemical method for generation and quantitative investigation of the physical and chemical properties of  $^1\text{O}_2$  in polymer films. Conceptually, our method (Scheme I) employs the following: (1) an endoperoxide ( $\text{EO}_2$ ) which may be solubilized in polymer films and which is capable of generating  $^1\text{O}_2$  thermally at convenient temperatures; (2) a singlet oxygen acceptor, A, which forms an adduct  $\text{AO}_2$  upon reaction with  $^1\text{O}_2$ ; (3) selection of adducts ( $\text{AO}_2$ ) which are capable of decomposing in the polymer with the production of a chemiluminescent product A. Quantitative measurement of the chemiluminescence intensity  $I_{\text{CL}}$  as

a function of the concentration of A ( $C_A$ ) at constant temperature provides information concerning physical properties (diffusivity) of  $^1\text{O}_2$  in the polymer film. Measurement of  $I_{\text{CL}}$  as a function of the addition of singlet oxygen quenchers (Q) at fixed  $C_A$  and temperature provides information concerning the chemical properties (reactivity) of  $^1\text{O}_2$  toward these quenchers in the polymer systems.<sup>2,3</sup>

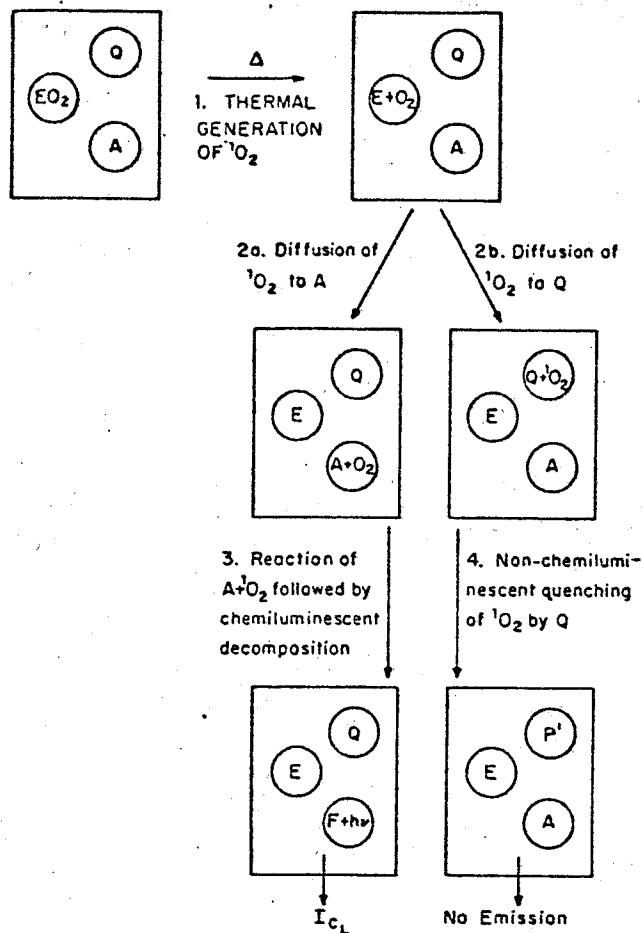
The compounds employed in this study are given in Scheme II. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) films were used as test matrixes to explore the feasibility of the method. Polymer films

(2) The high sensitivity toward measurement of chemiluminescence allowed the acquisition of statistically useful data over periods of time such that there was no experimental change in the measured intensity. For a discussion, see H. C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 282 (1974).

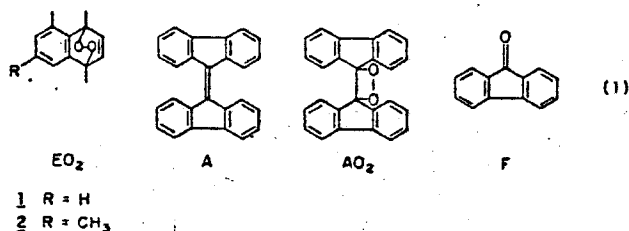
(3) For relevant work on the reactivity of singlet oxygen in polymers see: E. V. Bystritskaya and O. N. Karpukhin, *Dokl. Phys. Chem. (Engl. Transl.)*, **221**, 353 (1975); V. M. Anisimov, O. N. Karpukhin, and A. M. Mattuchi, *Dokl. Akad. Nauk SSSR*, **214**, 323 (1974); *Dokl. Phys. Chem. (Engl. Transl.)*, **214**, 93 (1974); E. V. Bystritskaya, E. V. Karpukhin, and O. N. Karpukhin, *Vysokomol. Soyedin., Ser. A*, **18**, 1969 (1976); *Polym. Sci. USSR (Engl. Transl.)*, **18**, 2242 (1976).

(1) (a) See "Singlet Oxygen Reactions with Organic Compounds and Polymers", B. Ranby and J. Rabec, Eds., Wiley, New York, 1978, for a comprehensive and recent review; (b) M. L. Kaplan and A. M. Trozzolo, "Singlet Oxygen", Academic Press, New York, 1979, p 575.

Scheme I

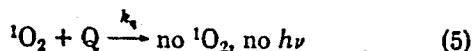
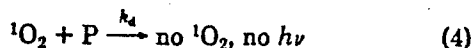
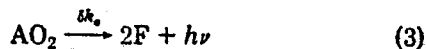
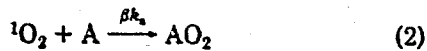
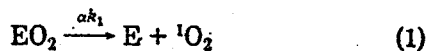


Scheme II



containing  $\text{EO}_2$  and A were found to be chemiluminescent, with the emission being experimentally indistinguishable from that of photoexcited fluorenone fluorescence. Fluorenone was detected as a reaction product by IR and TLC analysis.

**Kinetic Model for Analysis of Chemiluminescence Data.** Equations 1-5 (rate constants are given over the arrows)



represent the simplest series of steps necessary for analysis of our chemiluminescence data (see Scheme II for the structures which correspond to the symbols in the equations), where P is a hypothetical intrinsic polymer quencher that leads to an eventual unit quenching efficiency of  $^1\text{O}_2$  for each encounter of  $^1\text{O}_2$  and P.  $k_d$  and  $k_q$

are the rate constants for total  $^1\text{O}_2$  quenching by P and A.  $\beta$  is the fraction of  $^1\text{O}_2$  that is quenched by A and which leads to  $\text{AO}_2$ .  $\alpha$  and  $\delta$  are the quantum yields for  $^1\text{O}_2$  formation and for chemiluminescence from  $\text{EO}_2$  and  $\text{AO}_2$ , respectively. The quantities  $\alpha$ ,  $\beta$ , and  $\delta$  are assumed to be constant under the reaction conditions.

In the absence of a specifically added quencher, Q, the measured intensity of chemiluminescence ( $I_{\text{CL}}^0$ ) is predicted,<sup>4</sup> from steps 1-5, to be a function of the concentration of A as shown in eq 6, where  $C_A$  and  $C_P$  are the

$$I_{\text{CL}}^0 = \alpha k_1 [\text{EO}_2] \beta \delta k_s \frac{k_a C_A}{k_a C_A + k_d C_P} \quad (6)$$

concentrations of A and P, respectively, and where the unit of concentration is moles of substance per mole of monomer unit.

Conditions were found such that  $I_{\text{CL}}^0$  could be held constant, within the experimental error, for periods of 20 min or longer. Under these conditions the change in concentrations of  $\text{EO}_2$  and A are negligible and, therefore,  $[\text{EO}_2]$  and  $C_A$  are treated as constants.<sup>4</sup> For experimental convenience eq 6 may be transformed into eq 7

$$(I_{\text{CL}}^0)^{-1} = (I_{\text{CL}}^{\text{max}})^{-1} [1 + (k_d C_P / k_a) C_A^{-1}] \quad (7)$$

where  $I_{\text{CL}}^{\text{max}}$  is equal to  $2\beta\delta k_1 k_s [\text{EO}_2]$ . If the above discussion is a valid description of the system, at high concentration of A (i.e.,  $C_A \rightarrow \infty$ ),  $I_{\text{CL}}$  approaches a limiting value ( $I_{\text{CL}}^{\text{max}}$  in eq 7).

Equation 7 predicts a linear relationship between  $(I_{\text{CL}}^0)^{-1}$  and  $C_A^{-1}$  and identifies the slope of such plots with  $(k_d C_P) / k_a$ . Indeed, experimental plots of  $(I_{\text{CL}})^{-1}$  vs.  $C_A^{-1}$  are linear (Figure 1).

In the presence of a specifically added quencher, Q, the chemiluminescence intensity is reduced from an initial value ( $I_{\text{CL}}^0$ ) to a value dependent on the concentration of Q ( $I_{\text{CL}}^Q$ ). From eq 1-5 a Stern-Volmer equation may be derived:

$$\frac{I_{\text{CL}}^0}{I_{\text{CL}}^Q} = 1 + \left[ \frac{k_q}{k_a C_A + k_d C_P} C_Q \right] \quad (8)$$

where  $C_Q$  is the concentration of quencher in the polymer.

The quantity  $(k_d C_P)^{-1}$  corresponds to the inherent  $^1\text{O}_2$  lifetime in the polymer in the absence of A and Q. If this quantity is known, then the rate constants for quenching ( $k_q$ ) by Q is given by

$$k_q = \frac{k_q}{k_a C_A + k_d C_P} \left( C_A + \frac{k_d C_P}{k_a} \right) \left( \frac{k_a}{k_d C_P} \right) k_d C_P \quad (9)$$

or

$$k_q = H(C_A + S)S^{-1}C_P k_d$$

where  $H$  is the slope of eq 8 and  $S$  is the ratio of slope to intercept of eq 7.

Equation 6 predicts a linear relationship between  $(I_{\text{CL}})^{-1}$  and  $C_A^{-1}$ , as is confirmed experimentally (Figures 1 and 2). Equation 7 predicts a linear dependence relationship between  $I_{\text{CL}}^0 / I_{\text{CL}}^Q$  and  $C_Q$ , as is confirmed experimentally (Figure 3a for Cyasorb as quencher and Figure 3b for Rylex as quencher).

From data of the type given in Figures 1-3 and eq 7 and 9, the relative reactivities for quenching of  $^1\text{O}_2$  were determined.<sup>5</sup> The latter are summarized in Table I.

(4) (a) H. C. Steinmetzer, P. Lechtken, and N. J. Turro, *Liebigs Ann. Chem.*, 1984 (1973); (b) N. J. Turro, M.-F. Chow, and M. Balustein, *J. Am. Chem. Soc.* 100, 7110 (1978); (c) *ibid.*, 102, 5053 (1980).

(5) J. R. MacCollum and A. L. Rudkin, *Eur. Polym. J.*, 14, 655 (1978).

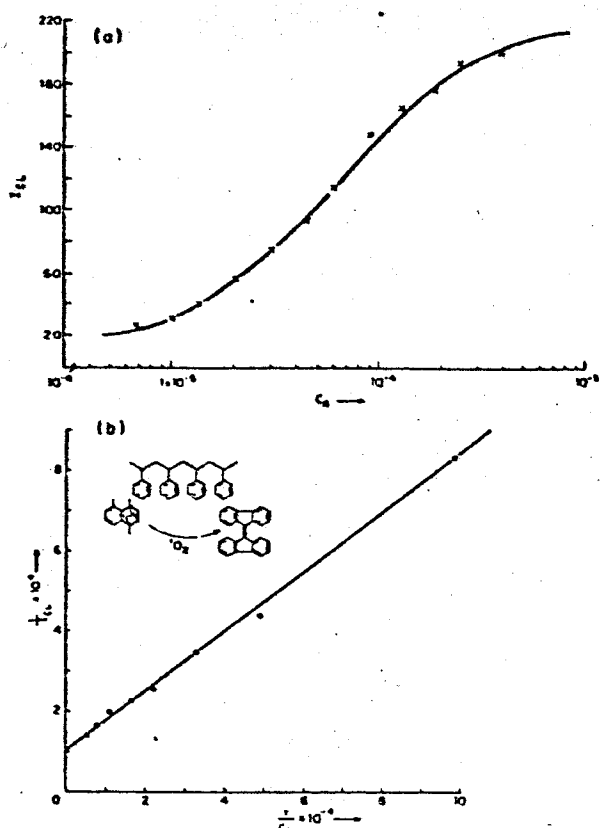


Figure 1. Experimental and theoretical variation of chemiluminescence intensity  $I_{CL}$  as a function of  $^1O_2$  acceptor concentration,  $C_A$ , for polystyrene films. Curve a shows the data (X) as a plot of  $I_{CL}$  vs.  $C_A$  and a theoretical fit of eq 7 (before inversion). Curve b shows the data (●) as a plot of  $(I_{CL})^{-1}$  vs.  $C_A^{-1}$  and the least-squares fit.

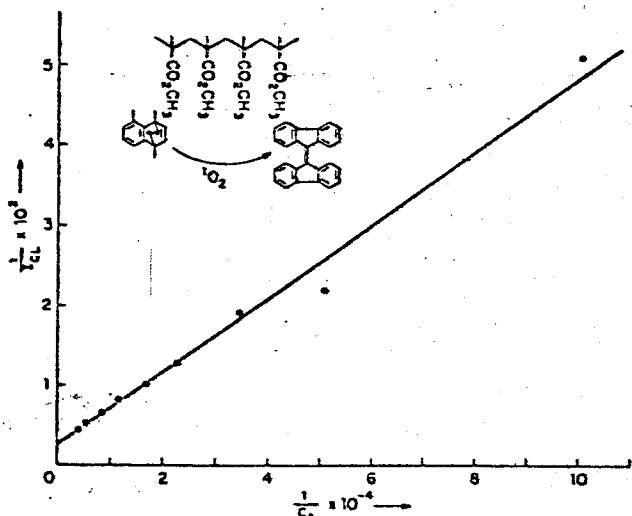


Figure 2. Plot of  $(I_{CL})^{-1}$  vs.  $C_A^{-1}$  for poly(methyl methacrylate) films.

Control experiments demonstrated for the concentration range employed that added quenchers did not diminish significantly the fluorescence of photoexcited fluorenone. Thus, the decrease in chemiluminescence intensity upon addition of quencher must be ascribed to some other factor, i.e., interception of  $^1O_2$ . For example, in polystyrene films Cyasorb ( $3 \times 10^{-3}$  M) quenches less than 5% of the emission from photoexcited fluorenone. In contrast, the same concentration is sufficient to quench 70% of the chemiluminescence produced by the  $EO_2/A$  system in polystyrene films.

As a check of the validity of the chemiluminescence method, rubrene replaced A as a singlet oxygen acceptor. The disappearance of rubrene was monitored (UV/visible

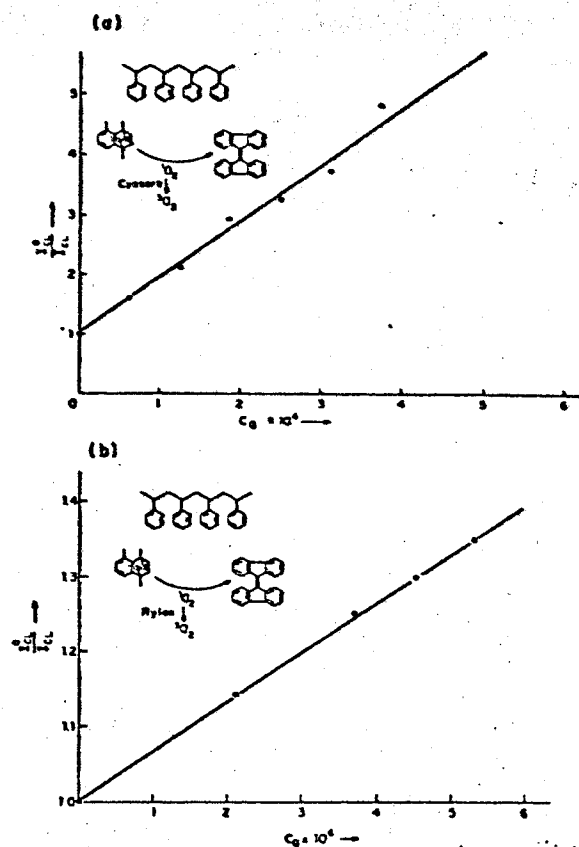


Figure 3. Stern-Volmer plots for the quenching of chemiluminescence in polystyrene films by (a) Cyasorb and (b) Rylex.

spectrometry) in the presence and the absence of quenchers. The efficiency of rubrene disappearance was measured, and the data were treated by a Stern-Volmer relation

$$\Phi_0/\Phi_q = 1 + k_q \tau C_q \quad (10)$$

where  $\Phi_0$  and  $\Phi_q$  are the conversion of rubrene in the absence and the presence of quencher whose concentration is  $C_q$ , respectively. The singlet oxygen lifetime at a fixed (initial) concentration of rubrene is  $\tau$ . From such measurements, with Rylex and Cyasorb as additives, the ratio of rate constants for quenching of  $^1O_2$  by these quenchers could be evaluated as 6.8. This value is in excellent agreement with that (Table I, 6.5) determined by the chemiluminescence method. No evidence was obtained for a catalytic or complicating destruction of the endoperoxide by Rylex or by Cyasorb. Also, since the absolute quantities of these quenchers was small relative to the endoperoxide, and since diffusion of the peroxide and the quencher are strongly inhibited, in the worst case only a small percentage of the total peroxide would be affected.

#### Discussion

From the plot of  $I_{CL}^0$  as a function of  $C_A^{-1}$ , the magnitude of  $C_p k_d/k_a$  is computed to be  $7 \times 10^{-5}$  M for polystyrene at  $45^\circ C$ . Under an assumption that the total quenching of  $^1O_2$  by A is diffusion controlled in the polymer (i.e.,  $k_d/k_a = 1$ ), the value of  $C_p$  is computed to be  $7 \times 10^{-5}$  M. From the exciton migration model,<sup>6</sup> the

(6) (a) G. Geuskens, "Comprehensive Chemical Kinetics", Vol. 14, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, 1975, p 333; N. J. Turro, *Pure Appl. Chem.*, 49, 405 (1977); (b) H. C. Wolf, *Adv. At. Mol. Phys.*, 3, 119 (1967); W. Klopffer, N. J. Turro, M.-F. Chow, and Y. Noguchi, *Chem. Phys. Lett.*, 54, 457 (1978); (c)  $K_d$  is defined as the diffusion rate constant between  $^1O_2$  and an intrinsic polymer quencher. It is assumed that the total quenching of  $^1O_2$  by A is diffusion controlled; i.e.,  $P = 1$ .

TABLE I: Quenching of  $^1\text{O}_2$  in Polystyrene Films

| quencher                        | polystyrene                                     |                   | fluid soln                                     |                   | rate constant<br>(fluid soln)/<br>rate constant<br>(styrene) |
|---------------------------------|---|-------------------|--|-------------------|--|
|                                 | rate constant,<br>$\text{M}^{-1} \text{s}^{-1}$ | rel<br>reactivity | rate constant                                  | rel<br>reactivity |  |
| Rylex <sup>a</sup>              | $4.4 \times 10^4$                               | 1300              | $4.3 \times 10^3$ (toluene)                    | 4300 <sup>b</sup> | 10   |
| Cyasorb <sup>a</sup>            | $6.2 \times 10^7$                               | 200               | $4.0 \times 10^3$ (toluene)                    | 400 <sup>b</sup>  | 6  |
| nickel(II) bis(acetylacetonate) | $4.9 \times 10^4$                               | 15                | $3 \times 10^3$ (toluene)                      | 300 <sup>b</sup>  | 61   |
| 9,10-dimethylantracene          | $2.9 \times 10^4$                               | 9                 | $3.0 \times 10^7$ (benzene)                    | 30 <sup>d,e</sup> | 10   |
| 9-methylantracene               | $1.1 \times 10^4$                               | 3                 | $3.0 \times 10^4$ (benzene)                    | 3 <sup>d</sup>    | 2.7  |
| 2,5-diphenylfuran               | $8.4 \times 10^5$                               | 2.5               | $8.6 \times 10^7$ ( $\text{CH}_2\text{Cl}_2$ ) | 90 <sup>c</sup>   | 102  |
| 9,10-diphenylantracene          | $3.3 \times 10^4$                               | 1                 | $1.0 \times 10^4$ (benzene)                    | 1 <sup>d</sup>    | 3  |

<sup>a</sup> Cyasorb and Rylex are the commercial names for (*n*-butylamine)nickel(II) bis[2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenoxy]] and nickel(II) di-*n*-butyldithiocarbamate, respectively. <sup>b</sup> A. Zweig and W. A. Henderson, Jr., *J. Polym. Sci., Polym. Chem. Ed.*, 13, 717 (1975). <sup>c</sup> D. R. Brewer, III, Ph.D. Thesis, Georgetown University, Washington, DC, 1974. <sup>d</sup> B. Stevens, S. R. Perez, and J. A. Ors, *J. Am. Chem. Soc.*, 96, 6846 (1974). <sup>e</sup> B. Stevens and J. A. Ors, *J. Phys. Chem.*, 80, 2164 (1976).

"number of hops",  $n$ , made by an exciton through a polymer during its lifetime is given by  $n = C_P^{-1}$ . We now associate the "hop" of an exciton between polymer units with the translational displacement of  $^1\text{O}_2$  between two pendant monomers of a given (average) separation. From the data of Figure 2b,  $n = 1.43 \times 10^4$  for  $^1\text{O}_2$  in PS. Thus, the "range",  $l$ , of diffusion<sup>7</sup> of  $^1\text{O}_2$  in PS is evaluated as 660 Å. Similar treatment of data for PMMA yields a value of 420 Å. With the assumption that the diffusivities of  $^1\text{O}_2$  and  $^3\text{O}_2$  are similar, we may evaluate<sup>8b</sup> the lifetime,  $\tau$ , of singlet oxygen from the equation  $l = (3D\tau)^{1/2}$ , where  $D$  is the diffusion coefficient of  $^3\text{O}_2$ . Taking our experimental values of  $l$  and literature values<sup>5</sup> of  $D$ , we calculate that  $\tau(^1\text{O}_2)$  is  $135 \times 10^{-6}$  and  $430 \times 10^{-6}$  s in PS and PMMA, respectively. These values fall in the range of literature values reported for the lifetime of  $^1\text{O}_2$  in fluid solutions:<sup>8</sup>  $10 \times 10^{-6}$ – $1000 \times 10^{-6}$  s. Furthermore, our values of  $\sim 500$ – $600$  Å are comparable with findings that  $^1\text{O}_2$  can diffuse up to 500 Å in stearate monomolecular films.<sup>9</sup> Once the singlet oxygen lifetime,  $(C_P k_q)^{-1}$ , was determined, the absolute value of  $k_q$  was calculated and is summarized in Table I.

The ratio of quenching constants for Rylex and Cyasorb derived from the ratio of slopes in Figure 3 is  $\sim 7$  ( $6.7 \times 10^4$  vs.  $9.4 \times 10^3$ ). The ratio of rate constants for these quenchers in fluid solution is  $\sim 30$  ( $5 \times 10^9$  vs.  $1.6 \times 10^8$ ). This difference is attributable to a "leveling" effect of the polymer medium on relative quenching rates. However, the leveling effect of the polymer may not be the sole factor which causes a reduction of the measured rate constant relative to fluid solution. The data in Table I confirm comparable reports in the literature.<sup>10</sup>

The conformity of our data and conclusions with those derived from three completely independent sources of measurement is substantial support for the validity of the proposed mechanism. The measurement of relative quenching constants for  $^1\text{O}_2$  in polymers now is a relatively straightforward matter. It will be of interest to study the quenching effectiveness of "physical" and "chemical" quenchers of  $^1\text{O}_2$  in polymers and to compare these results with those obtained from liquid-phase experiments. Such

investigations are now in progress and will be reported in due course.

### Experimental Section

**Purification of Polystyrene (PS), Poly(methyl Methacrylate) (PMMA), and Quenchers.** PS and PMMA were obtained from Polysciences. The polymers were purified by precipitation from methanol 3 times with benzene used as cosolvent. 2,5-Diphenylfuran, 9,10-dimethylantracene, 9-methylantracene, and 9,10-diphenylantracene were obtained commercially (Aldrich). The organic quenchers were purified by passage through neutral alumina (Baker analyzed reagent) in methylene chloride solvent and subsequently recrystallized from hexane. Rylex and Cyasorb were obtained from Dr. Bruce Monroe of Du Pont, and Nickel(II) bis(acetylacetonate) was obtained from Pfaltz and Bauer. The various complexes were used as received.

**Preparation of Bis(2,2'-biphenylene)ethylene.** Bis(2,2'-biphenylene)ethylene was prepared as follows. A benzene solution (100 mL) containing 4 g of Na and 14 g of fluorenone (Aldrich) was stirred at 40 °C for 20 h. A benzene solution (50 mL) containing 4 mL of  $\text{TiCl}_4$  was added to the reaction solution ( $\text{N}_2$  atmosphere), which was then stirred under  $\text{N}_2$  for an additional 15 h at 40 °C. The solution mixture was filtered, and 500 mL of methanol was added to the filtrate causing precipitation of bis(2,2'-biphenylene)ethylene. The precipitate was washed with an additional 500 mL of methanol and chromatographed by passage through neutral alumina ( $\text{CCl}_4$  solution). The overall yield of bis(2,2'-biphenylene)ethylene was 30%.

**Preparation of 1,4,8-Trimethylnaphthalene.**<sup>11</sup> Two moles of Na was added to ca. 800 mL of  $\text{NH}_3$  at  $-78$  °C.  $\text{Et}_2\text{O}$  (100 mL) was added to the  $\text{NH}_3$  solution until all of the Na dissolved. A solution of 87 g of 1-methylnaphthalene (Aldrich, purified by passage through neutral alumina) in 200 mL of  $\text{Et}_2\text{O}$  was added dropwise over 30 min. The reaction mixture was then allowed to stand for 30 min with the temperature maintained at  $-78$  °C. Stirring of the solution was maintained during the whole procedure. Two moles of  $\text{CH}_3\text{I}$  in 125 mL of  $\text{Et}_2\text{O}$  was then added dropwise to the reagent solution. The  $\text{NH}_3$  was allowed to evaporate over a 20-h period at room temperature. The  $\text{Et}_2\text{O}$  solution was washed with 200 mL of  $\text{H}_2\text{O}$  (3 times) and dried over 4-Å molecular sieve. A nearly quantitative yield of 1,4,8-trimethyl-1,4-dihydronaphthalene was collected. 1,4,8-Trimethyl-1,4-dihydronaphthalene (98 g) mixed with 2 g of 10% Pd on carbon was heated at 250 °C for 60 h under a  $\text{N}_2$  atmosphere. The

(7) The  $l$  is the value of the end-to-end distances of random walks in  $n$  hops, according to  $l = an^{1/2}$ , when  $a$  is the average separation distance between nearest-neighbor monomers and is taken to be 5.5 Å for PS.

(8) C. S. Foote, "Singlet Oxygen", H. Wasserman, Ed., Academic Press, New York, 1979, p 139.

(9) B. Schnuriger, J. Bourdon, and J. Bedu, *Photochem. Photobiol.*, 8, 361 (1968).

(10) E. V. Bystritskaya and O. N. Karpukhin, *Akad. Nauk. USSR, Engl. Trans.* 221, 353 (1975). The derived quantities in this paper are based on M units. Conversion to mole fraction units is necessary for a direct comparison, i.e., so that the ratio  $k_q/k_d$  is unitless.

(11) H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, 253 (1972).

organic fraction was extracted with ca. 90 mL of benzene. The low-boiling material and the benzene were removed by vacuum distillation at 50 °C and 3 torr. Sublimation of the residue at 90 °C and 3 torr provided ca. 60 g of 1,4,8-trimethylnaphthalene. The overall yield is 60%.

**Preparation of 1,4,8-Trimethylnaphthalene 1,4-Endoperoxide.** A methylene chloride solution (20 mL) containing 1 g of 1,4,8-trimethylnaphthalene and 2 mg of methylene blue was irradiated with a tungsten lamp for 5 h. Oxygen was bubbled through the solution during the irradiation. The reaction solution was then passed through dry Alumina column. The column was then washed with extra 30 mL  $\text{CH}_2\text{Cl}_2$ . The solutions were concentrated to ~20 mL. The endoperoxide was then crystallized by adding 50 mL of hexane at -78 °C: yield, 70%; NMR ( $\text{CCl}_4$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  1.76 (s, 3 H), 1.8 (s, 3 H), 2.5 (s, 3 H), 6.5 (s, 2 H), and 7 (m, 3 H).

**Preparation of Polymer Films.** A 1.5-mL benzene solution of 0.25 g of PS and PMMA and an appropriate amount of bis(2,2'-biphenylene)ethylene (when appropriate) singlet oxygen quencher was mixed by rotation for 2 h at room temperature in an aluminum foil covered vial, after which 0.074 mmol of trimethylnaphthalene endoperoxide was added to the vial, and rotation was continued for another 30 min. Typically, 0.76  $\mu\text{mol}$  of bis(2,2'-biphenylene)ethylene was employed for quenching studies. The benzene solution was spread on a glass slide with a glass frame on the edge. The slide was placed in a dark box for 4 h before drying in vacuo. The thickness of the dry film was ca. 180  $\mu\text{m}$ . A portion of a dry film was sandwiched between an aluminum foil wrapped stainless-steel block and a thin stainless-steel strip having a hole 8 mm in diameter. The sample was degassed at  $10^{-2}$  torr (stored under an argon atmosphere).

**Identification of Products.** The polymer film was heated at  $50 \pm 5$  °C for 20 h under an argon atmosphere. The film was then dissolved in methylene chloride, and the products were analyzed by TLC. Fluorenone and

trimethylnaphthalene were the only detectable products. The structure of the fluorenone product was corroborated by extraction from the TLC plate and comparison with an authentic sample (IR).

**Determination of the Chemiluminescence Spectrum Produced by Reaction of  $^1\text{O}_2$  with Bis(2,2'-biphenylene)ethylene.** The film containing naphthalene endoperoxide and bis(2,2'-biphenylene)ethylene was heated at 65 °C under an argon atmosphere. A chemiluminescence spectrum was recorded with a Perkin-Elmer MPF-3L spectrophotometer equipped with a Hamamatsu 777 phototube or a Centronic P4283TIR phototube. The chemiluminescence spectrum was identical with photoexcited fluorenone fluorescence under comparable conditions.

**Systematic Measurement of Chemiluminescence Intensity as a Function of Bis(2,2'-biphenylene)ethylene (and Singlet Oxygen Quencher).** The polymer film was maintained at  $47 \pm 0.5$  °C and kept under an argon atmosphere throughout the quantitative chemiluminescence measurements. The chemiluminescence was detected by a Centronic P4283 TIR phototube. The signal derived from the phototube was amplified by an Ortec 471 spectroscopy amplifier and 550 SCA and stored in a Tracor Northern MCA. There was no experimentally detectable change in the measured chemiluminescence intensity over a 20-min period.

**Treatment of the Data.** The intensity was the average of measured intensity over 20-min, over which there was no experimental change in the measured intensity. The intercept and the slope were determined by least-squares fitting. The solid line shown in the figures is a calculated line based on experimental data. The unit of concentration was converted to mol/L, which was used in Table I. The density of polystyrene was adapted as 1.05.

**Acknowledgment.** We thank the Air Force Office of Scientific Research, the National Science Foundation, and the IBM Corp. for their generous support of this work.